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OBSERVATION OF METALLIC CONDUCTIVITY IN LIQUID CARBON

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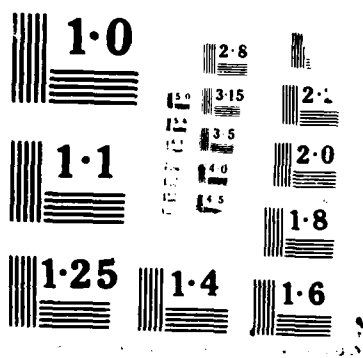
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<p>The temperature dependence of the electrical resistivity of carbon fibers has been measured at atmospheric pressure and for temperatures up to and above the melting point at 4450 Kelvin. Vapor-grown graphite fibers of different crystalline perfection were heated with electrical pulses 28 microseconds in duration. The transient reflectivity of graphite irradiated with picosecond laser pulses was also measured and the results show evidence for nonequilibrium heating. From this work, it is concluded that liquid carbon is metallic with a nearly temperature independent electrical resistivity of 30 micro-ohm centimeters.</p>			
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OBSERVATION OF METALLIC CONDUCTIVITY IN LIQUID CARBON

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ABSTRACT

We report the temperature dependence of the electrical resistivity of carbon at atmospheric pressure and temperatures up to and above the melting point at $4450 \pm 100\text{K}$. Vapor-grown graphite fibers of different crystalline perfection were heated with $25\mu\text{sec}$ electrical pulses. We also measure the transient reflectivity of graphite irradiated with picosecond laser pulses and find evidence for nonequilibrium heating. We conclude that liquid carbon is metallic with a nearly temperature independent electrical resistivity of $20 \pm 1 \mu\Omega/\text{cm}$.

Recently, there has been disagreement about whether graphite, molten under pulsed laser irradiation [1], is an electrical insulator [2,3] or a conductive metallic liquid [4,5,6]. Unfortunately, optical probing techniques are complicated [5] by the emission of particles during pulsed laser melting of the graphite surface. The light which is used as a probe is scattered and absorbed by the emitted material. Measurements of the electrical resistivity of liquid carbon were reported that indicated liquid carbon is an insulator [3]. In contrast, we report a direct measurement of the electrical resistivity of liquid carbon in the high temperature ($T > 4500$ K), low pressure ($p \leq 60$ bar) range. We demonstrate that liquid carbon has an electrical resistivity of $\rho = 30 \mu\Omega\text{-cm}$, which is that of a nearly free electron liquid with 4 free electrons per atom. Hence we conclude that liquid carbon is a metal.

Bundy [7] has shown that liquid carbon is metallic ($\rho \sim 150 \mu\Omega\text{-cm}$) in the pressure regime $10 < p < 110$ kbar. Using similar graphite starting material, our low pressure results are consistent with those of Bundy [7]. In addition, Shaner [8] has reported a roughly constant electrical resistivity ($\sim 1000 \mu\Omega\text{-cm}$) for liquid carbon at 4 kbar and up to 6000 K. Collectively, these results obviate the need for having two distinct liquid phases (one conducting and one insulating) in the of the carbon (p, T) phase diagram [9,10].

We used pyrolytic graphite fibers grown by chemical vapor deposition [11] and each were subsequently heat-treated to a different temperature, T_{HT} , ranging from $2000 < T_{HT} < 3100$ K. For $T_{HT} \geq 3000$ K, the fibers are composed of 2-10 μm crystallites with three dimensional registry, while for $2400 < T_{HT} < 2600$ K the fibers exhibit in-plane order, but decreased c-axis registry. For $T_{HT} \leq 2000$ K, the structure has little long-range order. All fibers have the graphite c-axis preferentially aligned along the fiber radius, with the graphite planes running parallel to the fiber length [11]. The fibers are

mounted with flexible silver paint to the central electrodes of standard BNC copper connectors. The measurements are made in an ambient N_2 gas or N_2/SF_6 gas mixture. The fibers are heated using a single 28 μ sec current pulse of up to 20A. The current (measured across a 2.2 Ω shunt) and voltage across the fiber are monitored with oscilloscopes, and used to calculate the dissipated power and the fiber resistance as a function of time.

We have verified that our results are not due to arcing of the fibers, by monitoring both the temporal and spectral characteristics of the blackbody emission from the fibers. In addition to individual visible and ultraviolet (320 nm) detectors with nanosecond response times, we have recorded the time-integrated spectral emission by means of a multichannel spectrometer. We do not detect carbon emission lines at 247.8 nm, nor cyanogen lines which may signify plasma arcing. Furthermore, the time responses of both the visible and ultraviolet emissions are identical. Thus we claim our results are obtained from condensed carbon.

The c-axis thermal expansion coefficient [12] is four times the expansion along the a-axis. Because the fibers have an onion skin morphology [11] and large a-axis modulus (~ 400 GPa [12]), pressure could build up as the fiber is heated. However, fibers treated to 3100 K relax their structure and upon cooling a differential thermal contraction buckles the surface of the fibers (see Fig. 4 in [13]). In subsequent pulsed heating, thermal pressure can only build up between 3100 K and the melting point of graphite (4450 K [1-6]). As a result of the extended temperature interval between T_{HT} and melting, fibers heat treated to lower temperatures should build up more internal pressure during pulsed heating. The effects of differential thermal expansion should be more prominent for these fibers. The fact that we do not observe a significant difference in the resistivity of liquid carbon for fibers heat treated between 3100 and 2400 K suggests that thermal expansion

induced pressure is released by cracks forming in the outermost carbon layers. The dynamic vapor pressure exerted on the surface of the liquid upon melting may be approximated from the momentum conservation condition applied to the vaporizing material. Assuming that the entire fiber vaporizes in $3\mu\text{sec}$, we find that the pressure exerted on the liquid surface is $p \leq 40$ bar.

In Fig.1 we show the time dependence of the resistance measured on two typical fibers heat treated to 3100 K and 2000 K. For the fiber with $T_{HT}=3100$ K, the resistance reaches a maximum after $5\mu\text{sec}$ and saturates after $9\mu\text{sec}$. About 100kJ/mole are absorbed by the fiber before the resistance maximum is reached, and this is sufficient to raise the fiber temperature to the melting point. During the time between the resistance maximum and saturation, there is an additional $105 \pm 15\text{kJ/mole}$ absorbed. Since this is the value for the heat of fusion at 48kbar [7], we claim that the graphite fiber is melted by the current pulse. Similar results were obtained on fibers with $T_{HT}=2600$ and 2400 K. We measured about 20 fibers for each T_{HT} , with current densities differing by a factor of 4, and obtained very consistent results. The longevity of the fibers during the electrical pulse is further illustrated by the fact that a few fibers that melted during the pulse resolidified after the current was interrupted. The room temperature resistance of the resolidified fiber then differed from the resistance of the original fiber by less than 20%.

The simulated resistance time(temperature) responses shown in Fig.1 are generated by finite difference solutions of the Fourier heat flow equation[4]. The source term is the ohmic heating $I(t)^2 \cdot \rho_i(T)/(A_i)^2$, where I is the fiber current at time t and the fiber is modelled as a set of series resistors of length ϵ , and resistivity $\rho_i(T)$. The cross-sectional areas(A_i) of the individual segments are varied sinusoidally from the mean cross-section by up to five percent to simulate actual variations in the fiber

diameter. This variation, modelled using discrete slabs, produces the series of steps seen in the simulated time dependence of the resistance between t_1 and t_2 in figure 1. The thermal conductivity and specific heat for solid graphite are calculated as in Ref.4. The current is calculated self-consistently by modelling the circuit as a 520V constant voltage source (for 28 μ sec) with an internal resistance of 48 Ω (including the shunt resistor and all wire resistances) in series with the fiber.

The temperature dependent electrical resistivity for graphite below the melting point is determined by matching calculated current and voltage curves to experimental curves for times between the beginning of the current pulse and the time when the resistance maximum is reached (or the end of the plateau for the $T_{HT}=2000$ K case). The fit uses the resistivity value of the fibers at 300K [14] and the melting point of graphite (4450 K [1-4]) as input parameters, and the heat of fusion is taken to be 105 kJ/mole[7]. The computer program adjusts the volume of the fiber and the cross-sectional area over length ratio (A/l , where A is the average over all A_i) and provides a calculated fiber length which is within 20% with the value we measure independently. The thermal properties of liquid carbon are determined using a Fermi gas model assuming 4 electrons per atom.[4] Figure 1 illustrates the exceptional quality of the simulation model.

In Fig.2 we plot the resistivity versus temperature for graphite fibers with different T_{HT} . The data we report for $\rho(T)$ on the fibers with $T_{HT}=3100$ K and 2600 K compare well with those previously reported for a graphite of the same density[15]. Multiplying the A/l ratio calculated for the solid by the resistance measured on the liquid fiber, we obtain a temperature-independent resistivity value for liquid carbon of $\rho = 30 \pm 8 \mu\Omega\text{-cm}$ for fibers with $T_{HT} \geq 2400$ K, and $\sim 70 \mu\Omega\text{-cm}$ for the fibers with $T_{HT}=2000$ K. This suggests that the crystalline perfection of the starting material influences the melting

process[8]. Shaner [8] reported a 100% expansion of highly disordered graphite rods upon melting. To justify our assumption of a constant A/l ratio, at least for the fibers with $T_{HT} > 2400K$, we note that the radial morphology of our fibers[11] is radically different from Shaner's carbon rods, and that we are using pyrolytic graphite instead of glassy carbon.

The contradiction between our data and that of Chauchard et al.[3] needs to be addressed. In figure 3 of their paper, Chauchard et al. report a time scale(~ 100 nsec) for the existence of the high resistance phase during laser heating, which is incompatible with the time given by the reflectivity measurements(~ 10 nsec) of Malvezzi et. al.[2]. The shape of the time dependent resistance reported in figure 3 suggests that the film was heated up over a time period that their oscilloscope could not resolve, and then cooled down slowly without necessarily undergoing a phase transition. Furthermore, in figure 2 of their paper, Chauchard et al.[3] find that the resistance of the graphite recovers its initial value after cooling and this is inconsistent with melting of films on the order of 100 nm thick (a few optical penetration depths). It has been shown [6] that under similar irradiation conditions, up to 100 nm of material can be lost to vaporization. Therefore, if Chauchard et. al.[3] had melted their films, they should observe an increase in the resistance after resolidification. While they neglect the temperature dependence of the solid phase resistivity, we believe the measurement of [3] is dominated by a solid layer of hot graphite in parallel with a relatively thin molten layer.

We have also performed time-resolved reflectivity measurements on HOPG at laser fluences three orders of magnitude below the melting threshold (140 mJ/cm^2 [2]) in an effort to address remaining contradictions. Our laser system produces ~ 5 psec duration pulses at a probing wavelength of 592.5 nm and a heating wavelength of 632.8 nm. The detector has a bandwidth of 10MHz,

and is preceded by an optical filter to remove scattered heating laser light. The average probing power is 1.5 mW and the heating power is 35 mW. The heating pulse energy of 0.15×10^{-9} J is focussed to a spot diameter of $\sim 10 \mu\text{m}$ and the energy density is at most 0.2 mJ/cm^2 .

Figure 3 shows the HOPG transient reflectivity measurements, accurate to within 10%, for various heating pulse energy densities produced by inserting absorption filters in the heating beam. The signal level at times prior to the heating pulse ($t < 0$) is the residual heating response from the preceding heating pulses, which occur every 4 nsec. During the heating pulse we observe an increase in the probe reflectivity, as expected theoretically but not observed by Malvezzi et al. [2]. This feature probably results from the formation of a solid state plasma and/or a non-equilibrium electron-lattice temperature which relaxes with a time constant shorter than the ~ 10 psec time resolution of our system. The ensuing decrease in reflectivity persists for several hundred picoseconds and corresponds to the slow diffusion of heat out of the illuminated volume[2]. We estimate a lattice temperature excursion of ~ 20 K and from our data we obtain a reflectivity derivative of $-5 \times 10^{-7} \text{ K}^{-1}$. This value is consistent with a Drude model for the slightly metallic conductivity of HOPG[12], which yields a temperature derivative of $-6.3 \times 10^{-7} \text{ K}^{-1}$. These observations demonstrate an important correlation between the temperature dependence of the conductivity and reflectivity of solid graphite, and a need for more careful consideration of the time-resolved reflectivity transients.

Finally, we estimate the electrical resistivity of liquid carbon by using a Fermi gas model with four electrons per atom. For a liquid density of $\sim 1.6 \text{ g/cm}^3$ [7], the free electron density is $n_e = 3.2 \times 10^{23} \text{ cm}^{-3}$ (free electron mass) and the Fermi velocity is $v_F = 2.5 \times 10^8 \text{ cm/sec}$. The Ziman theory for the conductivity of liquid metals [16] can be applied: We first use the Percus-

Yevick theory [17] to calculate the liquid structure factor, and the Heine-Abarenkov model [18] to estimate the model potential for carbon ions in the liquid. The electron mean free path can then be calculated [19] using the Ziman integral [16] and is 3.4 Å, roughly twice the interatomic distance. This yields a theoretical value for the resistivity of liquid carbon of 40 $\mu\Omega$ cm, in good agreement with the experimental value.

We conclude that near 4450K and close to atmospheric pressure, carbon undergoes a solid-to-liquid phase transition and the liquid carbon is metallic with a nearly temperature-independent electrical resistivity of 30 ± 8 $\mu\Omega$ -cm. This value is in reasonable agreement with theoretical estimates one can make from the theory of fully ionized liquid metals. More detailed discussions of the new data on the high temperature resistivity and the time-resolved reflectivity of solid graphite, and on the theory of electrical conduction in liquid graphite will be given in later publications.

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FIGURE CAPTIONS

Fig. 1 Time dependence of the resistance of two typical fibers. Also shown for each fiber is the simulated time dependent resistance we obtain from our model. According to our model, the fibers start to melt at time t_1 while t_2 is the time when more than 95% of the fiber is molten.

Fig. 2 Temperature dependence of the measured resistivity. The value for the resistivity of liquid carbon is the average over the values obtained on the fibers heat-treated ≥ 2400 K.

Fig. 3 Time dependent reflectivity of Highly Oriented Pyrolytic Graphite heated with a 5 picosecond heating pulse with the energy densities shown on the curves.

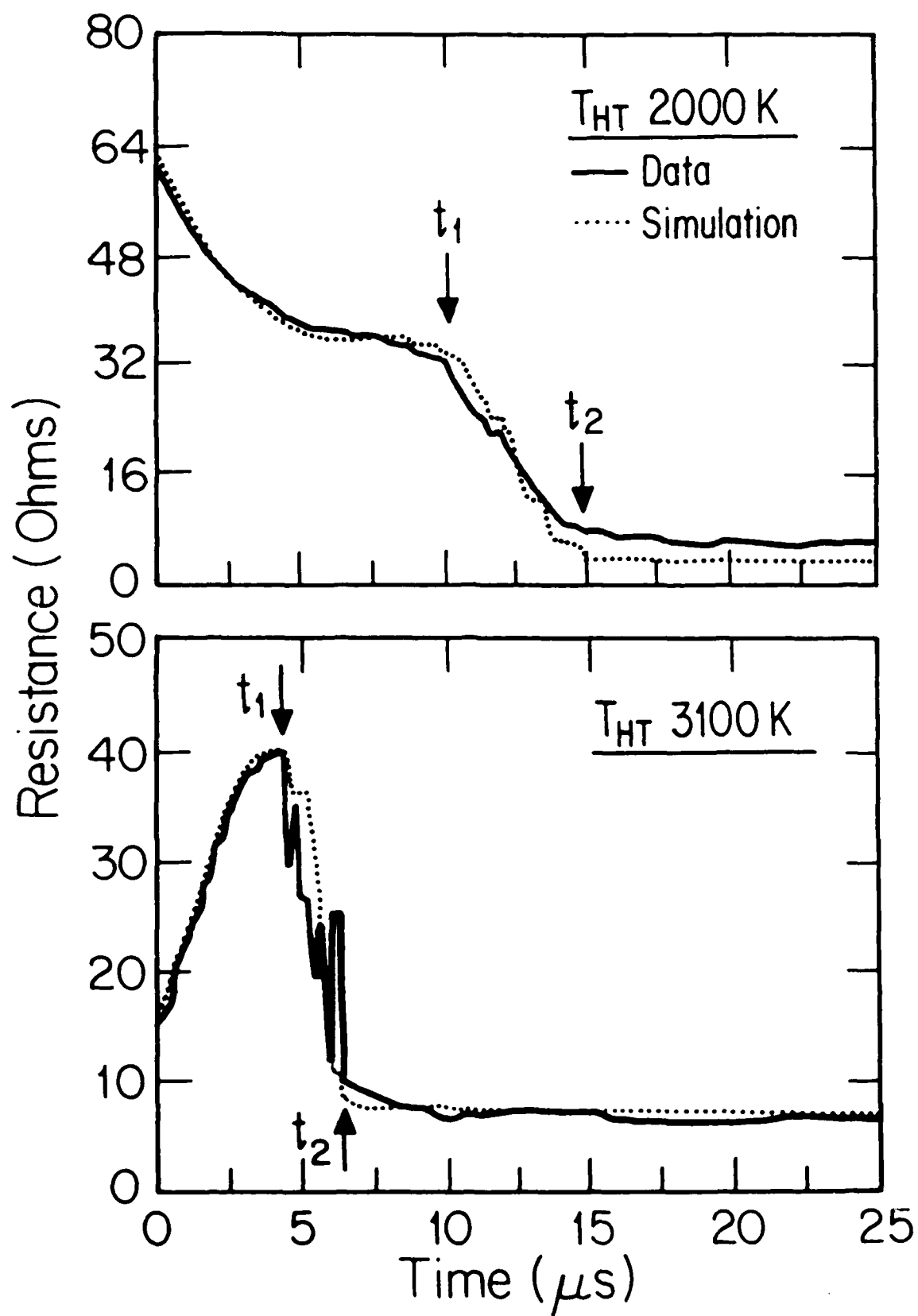


Fig 1

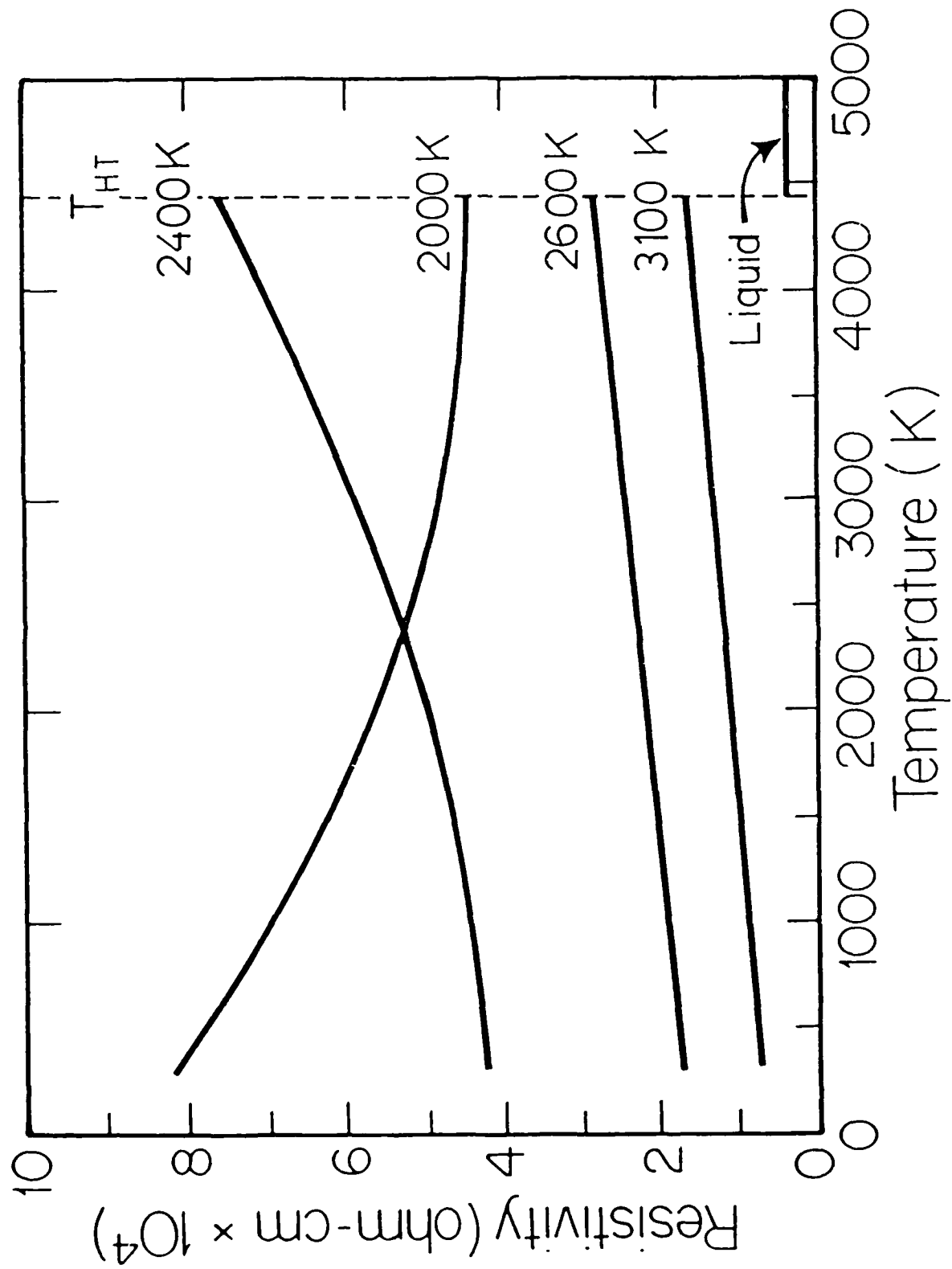


Fig 2

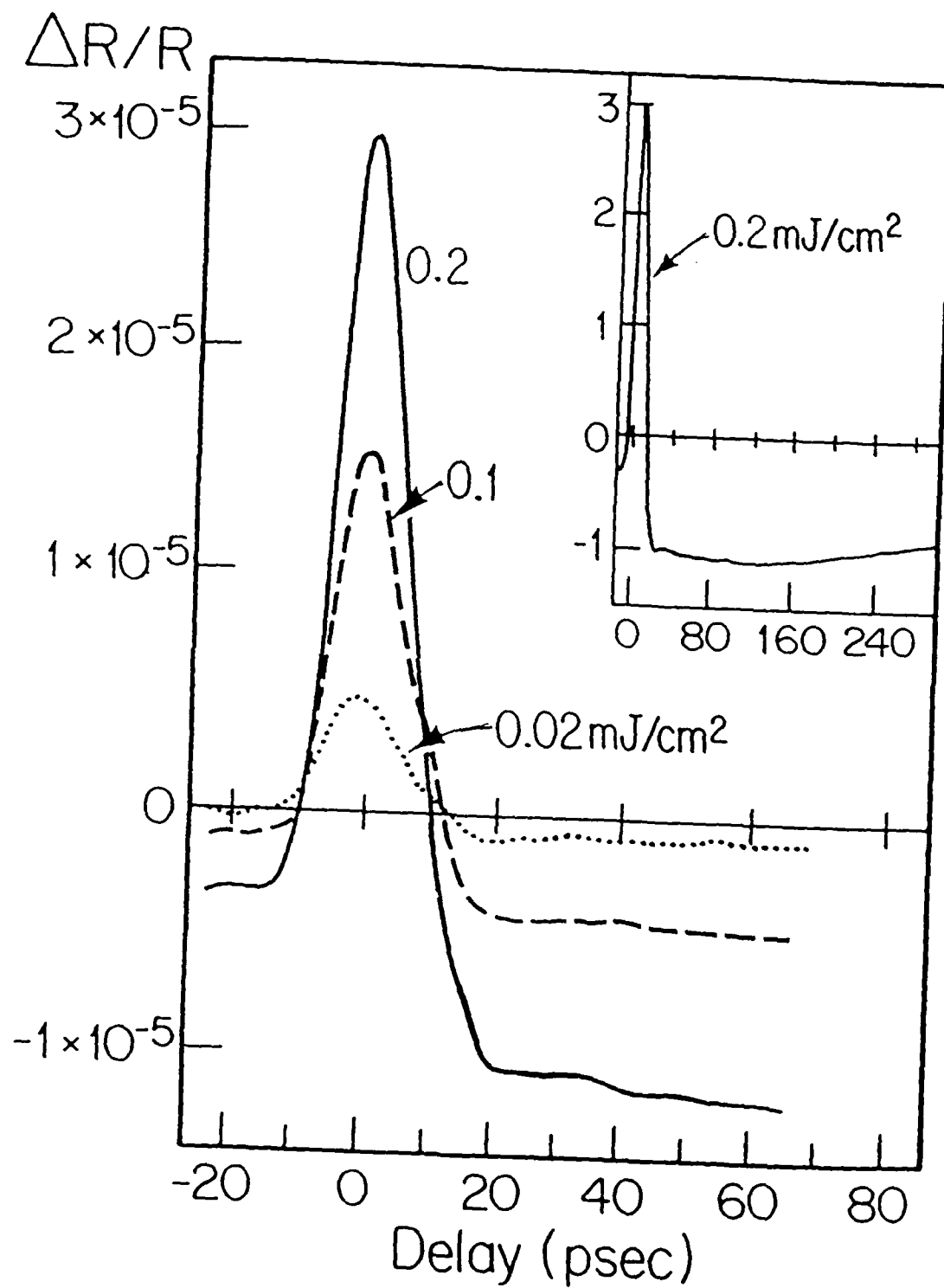


Fig 3

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